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Production of tool materials, in the circumstances of political risks

Introduction

Between 2013 and 2014 there were communications from the Commission addressed mainly to the European Parliament, but also a number of European organizations such as the Council, the Economic and Social Committee and the Committee of the Regions tackling the challenges in commodity markets and on raw materials. Critical materials are materials which are of great importance for the European Union, as they combine the risk associated with their acquisition [1]. A list of materials that are on the list of “critical materials” has been published [2]. It was determined that 20 materials are particularly important, because of the risk of supply shortage and due to their huge impact on the European economy. Such critical materials include, for example, antimony, beryllium, chromium, cobalt, niobium, indium, germanium, natural graphite, tungsten and others. Twelve of these materials to the present time cannot be recycled. As few metals of the platinum group are recovered at 35%, the remaining is recovered at the level of several percent. China is the country with the greatest impact on the acquisition of critical materials. There are also other countries, which focus on the production of certain elements in the metals, for example, in Brazil the niobium production amounts to 98% of world production. The European Union has decided to increase its activities aimed at freedom from monopolies and set different lines of action. These include:

- commencement of intensive mining in Europe,
- recycling of critical materials,
- the substitution of other materials with more accessible ones,
- reducing the share of critical materials in production.

The critical materials include cobalt and tungsten. These are the basic components of tool materials, Figure 1 [3]. The main producer of cobalt is the Central African Republic, which produces 56% of cobalt. European markets cobalt supplies are coming from Russia, satisfying 96% of European demand. The report [2] defines “Substitutability index” for cobalt is at 0.71 where the number 1 is assigned

to the materials with the lowest possible substitutions. Cobalt is recyclable in 16%. As many as 98% of tungsten in Europe comes from Russia, with 85% of the total world production based in China. As in the case of cobalt to tungsten substitutability index is 0.70 while the recycling 37%. Hardmetals tools use mainly sintered WC-Co. Although the polycrystalline diamond substrate is also used with the WC-Co and a binder phase for the diamond in an amount up to 8 vol%, Co. Tool materials for cutting tools drilling-bits are mainly based on diamond-cobalt composites. The data clearly indicate that almost half of the production tool materials in Europe depends on raw materials sourced in Russia. The greatest danger is, of course, halting tool materials by producers of raw materials as a result of political turmoil. Already the biggest inconvenience is the price volatility of cobalt, or rather continuous growth of price. Carbide is used in tool materials for metalworking, construction stone, plastic, asphalt, to drill rocks and geological exploration and many others applications.

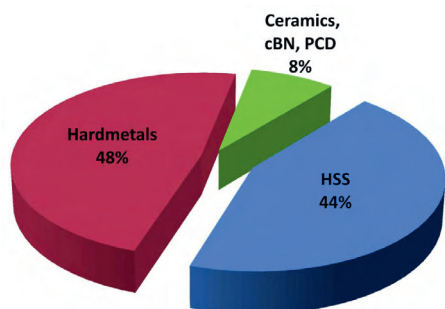


Fig. 1. The use of steels, ceramics and hardmetals in machining [3]

Our study was carried out in terms of reducing the share of tungsten carbide WC-Co compound used in the manufacture of materials for mining applications with input of cheaper phases or non-critical materials, but with the requirements for these materials, such as high abrasion resistance, high hardness, fracture resistance toughness, high strength, good thermal conductivity. The search for such materials is quite difficult due to the reactivity of the components with a WC-Co mixture. There are many types of hardmetals, they differ in cobalt content and involve other types of carbides, unfortunately, they are often included in the list of critical materials. The introduction of TiC, which is not a critical material, causes sparking tools, which excludes it from the application of this material in the mines, where methane is present, due to the possibility of an explosion. The other material with excellent tribological properties of SiC, though it affects the precipitation of graphite in the sintered WC-Co, which weakens the strength properties of the material. Hardmetals are produced using furnaces with the possibility of slight pressure use. Production in these devices is very efficient and profitable. A more advanced technology is the HIP – High isostatic pressing. At the moment, the FAST/SPS method creates new possibilities. The first studies on Spark Plasma Sintering technique suggested the presence of plasma during the process. Currently, mainly physicists withdraw from

the use of this name questioning the presence of plasma during the process, and use an acronym FAST Field Assisted Sintering Technology [4]. However, the SPS name is quite widely spread in many environments, especially in materials technologists and is still widely used. The difference between conventional sintering (resistance) and FAST lies in the fact that the other methods use alternating current, while in the FAST method periodically repeated current pulses lasting from several to several hundred milliseconds and with a magnitude of up to several thousand amps are used. The main advantage of using the sintering with a high-current DC pulse, so much more energy than other methods, is a very short duration of the process (up to several minutes). The current pulse can flow as a result of electrical discharges in the pores between the particles of the powder, resulting in the phenomenon of tunnelling through the oxide layer covering the powder or as a result of electric breakdown. In place of the formation of a neck there is a much higher temperature than inside the particle. In addition, the generated pressure is most often up to 50 MPa, which further improves the density of the material generated by increasing the contact surface between the sintered particles. Electrical discharges affect the clean surface of sintered particles, often through the phenomenon of evaporation at high temperatures arising in the points of contact of the particles, so that the activation occurs in these areas. This method allows the combination of materials, which were not obtained by other techniques, mainly due to the insufficient degree of compaction.

The paper presents the basic physical properties, hardness and fracture toughness of sintered material, obtained from a mixture WC-Co with Al_2O_3 addition.

Materials and experiment

The grain size of the powder mixture of WC-Co (YK15.6) was measured using a Shimadzu SA-CP3 apparatus. As a result of measurement for the powder obtained: for YK15.6 the average grain size (median) of 3.74 microns, the modal value of 3.53 microns and a surface area of 0.730 m^2/g . Producer of the YK15.6 mixtures is a Chinese company Chongyi Zhangyuan Tungsten Co. Ltd.

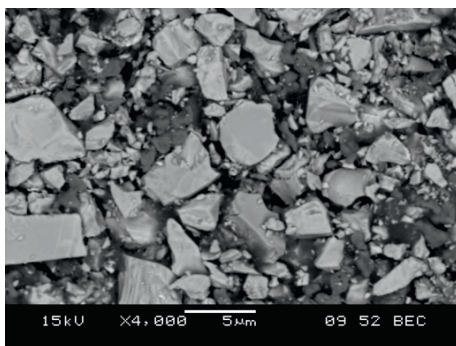
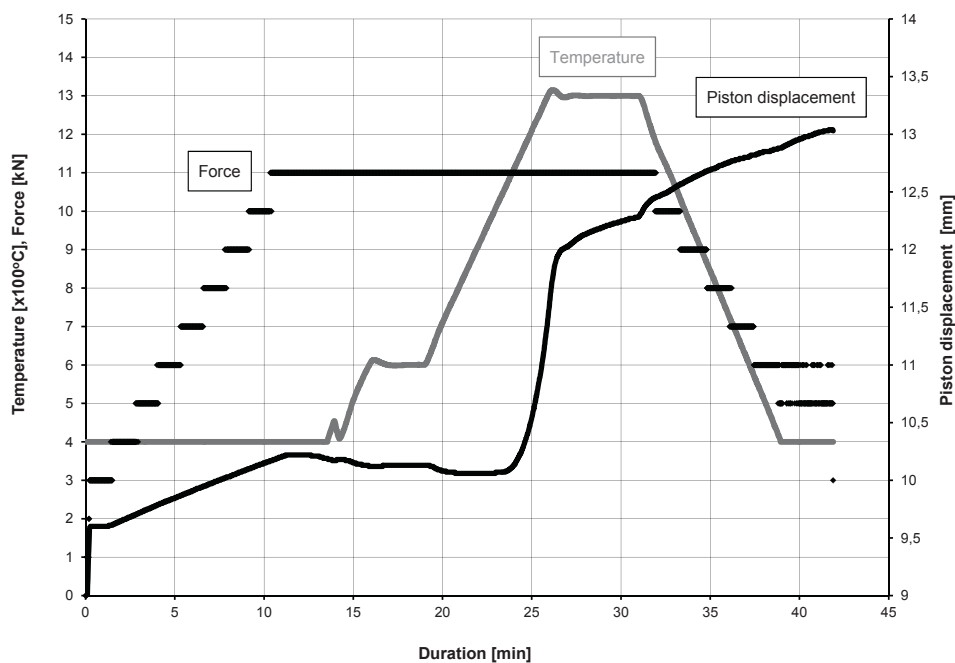


Fig. 2. Microphotography of the YK15.6 WC-Co powder

Tab. 1. Composition of the WC-Co mixtures according to the manufacturer's certificate

mixture designation	Elements								
	WC	Co	Fe	Ti	Mo	Nb	Ni	Cr	V
YK15.6	85.77	14.9	0.092	0.043	0	0.013	0.082	0.305	0

Conditions of the FAST/SPA process of sintering are presented in Figure 3.

**Fig. 3.** SPS curves of the sintering for YK15.6 powder with 10% Al_2O_3

The material was sintered in two stages to 600°C, withstanding for 3 minutes, and then at 1300°C for 5 minutes, at a pressure of 35 MPa. Heating and cooling speed was 200°C/min.

Tab. 2. Selected physical and mechanical properties for mixed powder WC-Co type YK15.6 with 10% of Al_2O_3

Sample	Apparent density ρ [g/cm ³]	The average value of Vickers hardness $\text{HV}_{30_{av}}$	Young Modulus E [GPa]	Poisson's ratio ν	Indentation fracture toughness $K_{Ic(HV)}$ [MPam ^{1/2}]
YK15.6+10% mas. Al_2O_3	10.99	1274	444	0.22	9.49

The obtained material was characterized by a relatively high hardness compared to the commercial material, for which the HV30 hardness is in the range of

1000. However, the suitability of the material for the cutting blades is determined by other properties such as abrasion resistance, thermal conductivity, toughness and more.

Conclusion

The use of modern methods of sintering SPS / FAST enables the consolidation of WC-Co powder and Al_2O_3 oxide phase.

Preliminary tests of sintered WC 15% Co and 10% Al_2O_3 confirm the possibility of obtaining a material with a higher hardness and fracture toughness relative to the surface of commercial materials.

References

- [1] Defining 'critical' raw materials – Raw materials- Enterprise and Industry. Retrieved from http://ec.europa.eu/enterprise/policies/raw-materials/critical/index_en.htm
- [2] Report on critical raw materials for the EU. Report of the Ad hoc Working Group on defining critical raw materials May 2014. Retrieved from http://ec.europa.eu/enterprise/policies/raw-materials/critical/index_en.htm
- [3] Kuzler F., *Advanced Arena: Why ceramic cutting tools?* Ceramic Industry 2012, 1.
- [4] Anselmi-Tamburini L.U., Kodera Y., Gasch M., Unuvar C., Munir Z.A., Ohyanagi M., Johnson S.M., *The effect of electric field and pressure on the synthesis and consolidation of materials: A review of the spark plasma sintering method*, J. Mater. Sci. 2006, 41, p. 3097.

Abstract

The problems of critical raw materials in the European Union, which are on a special list is presented. This group of materials includes cobalt and tungsten, which form the basis of tool materials. The article discusses key policy issues to minimize the risks associated with the use of these materials. As an example of beneficial new solutions for sintered WC-Co, it shows the addition of a 10% Al_2O_3 , sintered with SPS method.

Key words: tool materials, hardmetals, SPS, properties

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